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Particulars of KOKAI (Laid-Open) Specification

Patent KOKAI (Laid-Open) No. 102762/83
Laid-Open Date: June 18, 1983
Request for Examination: None
Patent Application No. 200861/81
Application Date: December 15, 1981
Convention Priority(ies): None
Inventor(s) Isao YOSEIMURA
Applicant: Asahi Dow Ltd.
Title of Invention:

Lower-temperature heat-shrinkable multilayered
barrier film and a process for preparing the same

SPECIFICATION

1. Title of the Invention:

Lower-temperature heat shrinkable multilayered
barrier film and a process for preparing the same

2. Claims:

(1) An oil-resistant lower-temperature heat-
shrinkable multilayered barrier film which is a four or
more-layered film comprising at least one layer of a blend
composition (ABC) layer consisting of

(A) at least one polymer selected from copolymers of
ethylene and monomers selected from vinyl-ester monomers,

aliphatic unsaturated monocarboxylic acids and alkyl esters of said monocarboxylic acids and linear low-density polyethylene,

(B) a soft elastomer, consisting of an ethylene- α -olefin copolymer and having a density of 0.91 g/cm^3 or below,

(C) either of crystalline polypropylene and crystalline polybutene-1 or a mixture thereof, said one layer being provided adjacent to a barrier layer which has a thickness constituting 35 to 5% of the total layer thickness and consists of a vinylidene chloride copolymer (PVD) having the crystal melting peak within the range of 140 to 155°C measured by using a differential scanning calorimetry (DSC), the surface layer of said film being provided with at least one resin (S) layer consisting of a polymer which consists mainly of linear low density polyethylene (LLDPE) selected from said polymer (A) and has the total thickness of 2 to 25 μ at a ratio of 5 to 40% to the total layer thickness, said barrier film having a heat shrinkage factor of at least 15 and 25% respectively at 70 and 80°C and the maximum value of shrinkage stress of at least 100 g/mm^2 .

(2) The multilayered barrier film according to claim (1), wherein said polymer (A) is an ethylene-vinyl acetate copolymer with a vinyl acetate content of 2 to 12 mol% and a melt index of 0.2 to 6.

(3) The multilayered barrier film according to claim

(1), wherein said polymer (A) is a polymer which is a copolymer of ethylene and at least one monomer selected from the group consisting of acrylic acid, acrylic acid esters, methacrylic acid and methacrylic acid esters and has a content of said monomer of 2 to 12 mole%.

(4) The multilayered barrier film according to claim (1), wherein said polymer (A) consists of the linear low-density polyethylene and has a melt index of 0.2 to 10 and a density of 0.910 to 0.935 g/cm³.

(5) The multilayered barrier film according to claim (1) or (4), wherein said polymer (A) is the linear low-density polyethylene prepared by copolymerizing ethylene with 7 mole% or less of at least one olefin selected from α -olefins of 3 to 12 carbon atoms such as propylene, butene, pentene, hexene, heptene, octene, 4-methyl-1-pentene and the like as the α -olefin.

(6) The multilayered barrier film according to claim (1), wherein said polymer (B) is a copolymer of 93 mole% or less and 40 mole% or more of ethylene and said α -olefin is selected from propylene, butene-1, 4-methyl-1-pentene and the like.

(7) The multilayered barrier film according to claim (1) or (6), wherein said polymer (B) is a soft copolymer which is prepared by randomly copolymerizing ethylene with an α -olefin and a small amount of polyenes and has a Vicat softening point of 80°C or below.

(8) The multilayered barrier film according to claim

(1), wherein said polymer (c) is a rigid polymer having a Vicat softening point of 100°C or above.

(9) The multilayered barrier film according to claim (1), wherein specific blending components forming the blend composition layer are at weight ratios of

$$0.90 \geq A/(A+B+C) \geq 0.20,$$

$$0.50 \geq B/(A+B+C) \geq 0.05 \text{ and}$$

$$0.50 \geq C/(A+B+C) \geq 0.05.$$

(10) The multilayered barrier film according to claim (1) or (9), wherein the specific blending components forming the blend composition layer are at weight ratios of

$$0.80 \geq A/(A+B+C) \geq 0.25,$$

$$0.40 \geq B/(A+B+C) \geq 0.10 \text{ and}$$

$$0.45 \geq C/(A+B+C) \geq 0.10.$$

(11) The multilayered barrier film according to claim (1), wherein said film is at least five-layered film having said blend composition (ABC) layers adjacent to both sides of the barrier (PVD) layer and further the resin (S) layers consisting mainly of the linear-low-density polyethylene (LLDPE) selected from the polymer (A) as surface layers on both sides of the blend composition (ABC) layers.

(12) The multilayered barrier film according to claim (1), wherein the high-temperature oil-resistant strength is at least 100 g/15 mm width at 95°C.

(13) A process for preparing a lower-temperature

heat-shrinkable multilayered barrier film comprising respectively melt kneading a blend composition (ABC) consisting of

(A) at least one polymer selected from copolymers of ethylene and monomers selected from vinyl ester monomers, aliphatic unsaturated monocarboxylic acids and alkyl esters of said monocarboxylic acids and linear-low-density polyethylene,

(B) a soft elastomer, consisting of an ethylene-clefin copolymer and having a density of 0.91 g/cm^3 or below,

(C) either of crystalline polypropylene, crystalline polybutene-1 or a mixture thereof, a vinylidene chloride copolymer (PVD) having the crystal melting peak within the range of 140 to 155°C measured by using a differential scanning calorimetry (DSC) and a resin (S) consisting of a polymer consisting mainly of linear-low-density polyethylene (LLDPE) selected from the polymer (A), providing at least one (ABC) layer adjacent to the (PVD) layer, providing at least one (S) layer on the surface layer, extruding the resulting 4 or more-layered tubular raw film through a multilayered die, quenching and solidifying the raw film with a liquid refrigerant, directly or heating the prepared film to 100°C or below and cold drawing said film at a drawing temperature within the range of 30 to 90°C at a surface area draw ratio of 4 or above and 30 or less, thereby to afford a drawn film comprising the PVD

layer having a thickness constituting 35 to 51 in the total layer thickness and the (S) layer having a total thickness of 2 to 25 μ at a ratio of to 5 to 40% the total layer thickness.

(14) The process for preparing the multilayered barrier film according to claim (13), wherein the drawing temperature is within the range of 35 to 80°C.

(15) The process for preparing the multilayered barrier film according to claim (13) or (14), wherein the drawing is carried out at a drawing temperature of 35 to 70°C and below the crystal melting point of the resins mainly constituting the respective layers.

(16) The process for preparing the multilayered barrier film according to any one of claims (13), (14) and (15), wherein the total layers are cold drawn at a drawing temperature of 35 to 70°C and below the Vicat softening points of the resins mainly constituting the respective layers thereby to impart cold drawing orientation to the total layers.

(17) The process for preparing the multilayered barrier film according to claim (13), wherein the drawing is carried out by using a rectifying contact guide for the purpose of substantially isolating the heating part from the drawing starting part, preparing a substantially independent temperature controlled air chamber while discontinuously contacting and removing a fluid and a laminate film thereof accompanied by the raw film and/or

film surface during drawing in the circumferential direction, stretching and drawing the film and deflating the drawn film simultaneously with the maximum diameter attained.

3. Detailed Explanation of the Invention:

This invention relates to a four or more-layered lower-temperature heat-shrinkable multilayered barrier film comprising a vinylidene chloride copolymer as a core layer. More particularly, it relates to a novel heat-shrinkable film having excellent various characteristics, such as lower-temperature heat shrinkage characteristics (shrinkage factor and shrinkage stress), low-temperature toughness, high strength of sealed parts (oil resistance, heat resistance and impact resistance at low temperatures of sealed parts), gas barrier properties, optical characteristics, such as transparency after heat shrinking, ply separation resistance, airtightness in clipping and the like. Uses thereof are not limited, and the film is usable for skin packaging, nonshrink packaging, flexible deep drawing packaging and the like in addition to shrink packaging.

As an example of uses thereof, the shrink packaging is taken and detailed hereinafter.

The presence of heat-shrinkable films for tightly shrink packaging contents is hitherto known for long. There have been various studies aiming at exhibi-

tion of characteristics of respective resins in a synthesized form by combining different kinds of resins and forming laminated films in requiring such films to show characteristics which cannot be displayed by single resins constituting the films.

Film characteristics for satisfying demands of the market, however, diverge too much, and demand characteristics have been enhanced. There are naturally limits to characteristics which can be exhibited by respective resins in a laminated state. Various restrictions are placed even on selection of laminable resins per se. If one of the characteristics is improved, deterioration may occur in the other. Any compromise must be inevitably made. As a result, gaps continue to increase between market demand and characteristics of existing films. Advent has been expected of films meeting such demand in the present situation.

For example, lower-temperature shrinkability and gas barrier properties have been required for particularly improving package finish of products and packaging products readily damaged by heat at present in especially the vacuum shrink packaging field, for example products of fatty foods, such as raw meat, processed meat, cheese or the like or products prolonging life by packaging while cutting off oxygen or the like. Since such contents are generally of nonuniform shape or there are often protrusions, such as bones or packaging containers or the

like, packaging must be carried out at a high shrinkage factor and stress with not only lower-temperature shrinkability in parts contacting packaged materials but also at a sufficiently lower temperature in parts out of contact therewith in order to obtain tight packages including the above-mentioned contents and the like. However, if the shrinkage characteristics are exhibited to a high temperature side or temperature dependence of shrinkage factor is great, i.e. in the case of films having shrinkage characteristics of rapidly shrinking at a certain temperature, phenomena of discoloring or deteriorating contents or uneven shrinkage due to temperature difference are caused, directly resulting in creases, sagging or the like. Thereby defects are often developed in that the surfaces of packages are hard to see or breakage will occur therein during transportation or the like.

Therefore, shrinkable films are required to have dimensional stability at a film preservation temperatures and exhibit shrinkage characteristics to the side of lower temperatures in shrink packaging and small temperature dependence. On the other hand, gas barrier properties are characteristics required for enhancing preservation quality of contents for a long period, and shrink packaging of particularly fatty foods cannot be considered in the absence of the characteristics.

However, there is nothing if films satisfying the above-mentioned two characteristics are opaque,

lusterless, opacifying (whitening) after heat shrinking, deteriorate strength of sealed parts or cause ply separation. On the one hand, since quality design of films having all the aforementioned characteristics is in considerable technical difficulty from the supplier side of laminated films, some of the characteristics are sacrificed in the present situation. On the other hand, films consisting of simple vinylidene chloride copolymer (hereinafter referred to as PVD) have well balanced performances, such as shrinkability, gas barrier properties, oil resistance, ligating properties or the like, and have been hitherto widely applied.

Films consisting of ordinary simple PVD, however, are yet insufficient for imparting sufficient shrinkability, and further deficient in satisfactory cold resistance, flexibility, heat sealability by heat or the like. Furthermore, plasticizers or stabilizers in especially large amounts must be added to impart extrusion stability, good stretchability in producing films, and the amounts are usually 6 to 10% by weight.

Since such plasticizers or stabilizers are unfavorable for sanitation and deficient in cold resistance and deteriorate film properties, particularly oxygen barrier characteristics, there are problems in that the thickness of barrier resins must be increased or the like. In order to even slightly solve the problems, there are methods for coextruding ethylene-vinyl acetate copolymer

(hereinafter referred to as EVA) with a vinyl acetate content, for example 28 and 18% by weight, and improved adhesive properties to PVD copolymer resin on both sides of the PVD copolymer containing 7 to 10% by weight of a plasticizer on the basis of weight to form three layers, drawing the resulting film and making the large amount of the plasticizer migrate from the layer consisting of the PVD copolymer, thereby improving barrier characteristics or the like. In such films, barrier characteristics are unstable with time and simultaneously deficient both in heat and oil resistance. Furthermore, there are problems, such as tendency to stickiness of films, insufficient modulus of elasticity or the like. Films are prepared by irradiating and crosslinking one side of such EVA (side sealed on the inside when formed into a bag) with electron rays in order to improve processing stability [Japanese Patent Application KOKAI (Laid-Open) No. 34565/72]. Such processes have disadvantages in being costly and complicated, difficult sealing of sealed parts rather than improving oil resistance by crosslinking and deteriorating high-temperature resistance and high-temperature oil resistance or the like.

As a method for partially improving the above-mentioned problems, Japanese Patent Application KOKAI (Laid-Open) Nos. 47079/77, 148577/77, 82888/78, 89945/81 and the like are known as methods for providing an EVA layer or low-density polyethylene layer on one side of a

PVD copolymer layer, and simple ionomer resin layer having a thickness of 20 to 50 μ through an EVA layer or directly a layer of a mixed ionomer resin and EVA on the vinyliden layer through a thin EVA layer with a high VAC content and a thickness of 0.2 to 3 μ on the other side stretching and orienting the resulting film under finely adjusted narrow temperature conditions, for example a heating temperature of 84 to 93°C, resulting from resin characteristics of the respective layers while keeping the PVD copolymer layer in an amorphous state, and crystallizing the stretched film. The processes for preparing films just described above are more facilitated than those already mentioned; however, stretching must be still carried out under conditions within a severe range, and optical characteristics tend to deteriorate between before and after use as compared with those in the processes previously mentioned. There are also problems in ply separation by entry of oil from cut surfaces of the films.

All of the aforesaid processes have respective characteristics and excellent; however, lower-temperature shrinkability is still insufficient with deficient heat resistance. Phenomena of opacifying (whitening) films are recognized when heated and highly shrunk. There is still deficiency in toughness properties at low temperatures.

As a result of research made on various resins, laminate constitution, and methods for stretching for a long period to overcome such phenomena, the present

inventor has finally completed this invention.

Thus, this invention consists as follows:

A four or more-layered film comprising at least one layer of a blend composition (AEC) layer consisting of

(A) at least one polymer selected from copolymers of ethylene and monomers selected from vinyl ester monomers aliphatic unsaturated monocarboxylic acids and alkyl esters of said monocarboxylic acids and linear low-density polyethylene,

(B) a soft elastomer, consisting of an ethylene- α -olefin copolymer and having a density of 0.91 g/cm^3 or below,

(C) at least one polymer selected from crystalline polypropylene and crystalline polybutene-1, said one layer being provided adjacent to a barrier layer of specific PVD, the surface layer of said film being provided with at least one resin (S) layer which consists mainly of linear low-density polyethylene (LLDPE) selected from said polymer (A) and has the total thickness of 2 to 25 μ at a ratio of 5 to 40% to the total layer thickness.

The process for preparing the film comprises highly stretching the respective layers at sufficiently lower-temperatures, i.e. below the crystal melting points of the resins which are a principal and secondary components of the aforesaid blend composition, preferably below the Vicat softening point (hereinafter referred to as VSP) of the blend composition.

The composition (A) in the aforementioned blend composition (ABC) layer is a relatively low crystalline polymer which is an almost intermediate between rigid and soft polymers and selected from the group of copolymers of ethylene and monomers selected from vinyl ester monomers, aliphatic unsaturated monocarboxylic acids and alkyl ester derivatives of the monocarboxylic acids and ethylene. Such a polymer preferably consists of ethylene-vinyl acetate copolymer (EVA), ethylene-ethyl acrylate copolymer (EEA), ethylene-methyl methacrylate copolymer (EMMA), ethylene-acrylic acid copolymer (EAA), ethylene-methacrylic acid copolymer (EMA) or a polymer (ionomer resin) wherein a polymer having carboxyl groups derived therefrom by partial saponification is at least partially converted into an ionomer. The amount of the monomers other than ethylene in the copolymers is preferably 2-12 mole%, more preferably 3 to 10 mole%. If the amount is 2 mole% or more, sealability, flexibility, transparency, respective strength characteristics and the like are improved. If the amount is 12 mole% or more, the copolymers may tend to have problems in poor extrusion processability, miscibility with other components and the like or in handleability by mutual blocking of surfaces when the copolymers form outer layers by processing into a film. The melt index of the resins in direct use as a raw material therefor is usually 0.2 to 10, preferably 0.3 to 5. If the melt index is 0.2 or below, there is a problem

in miscibility and extrudability of the raw material. If the melt index is higher than 10, strength as a base material may be insufficient. For example, a bubble undesirably tends to readily break in stretching or the like. Among them, EVA is most preferred for use as the blend composition layer, and the vinyl acetate group content thereof is preferably 3 to 8 mole%, more preferably 3 to 7 mole%. The linear-low-density polyethylene (LLDPE) refers to linear low-density polyethylene obtained by a medium-, low-pressure or, in some cases, high-pressure process, and prepared by copolymerizing 7 mole% or less, preferably about 1 to 5 mole% of especially at least one olefin selected from α -olefins of 3 to 12 carbon atoms, such as propylene, butene, pentene, hexene, heptene, octene, 4-methyl-1-pentene or the like as an α -olefin. The melt index thereof is preferably 0.2 to 10, and the density is preferably 0.910 to 0.935 g/cm³. The crystal melting temperature (mp) thereof obtained by a differential scanning calorimetry (DSC) (measured at a scanning speed of 10°C/min) is 110°C or above and up to 125°C and distinguished from the crystal melting temperature of 100 to 108°C of branched low-density polyethylene, having a density of 0.913 to 0.927 g/cm³ and prepared by an ordinary high-pressure process.

The thermoplastic elastomer (B) consisting of an ethylene- α -olefin copolymer refers to a soft copolymer of ethylene and one or more olefins selected from α -olefins

of 3 to 12 carbon atoms. In some cases, a small amount of a hydrocarbon having a polyene structure, for example dicyclopentadiene, 1,4-hexadiene, ethylidene-norbornene or the like may be further copolymerized. Propylene, butene-1, hexene-1, butene-1, 4-methyl-1-pentene, octene-1 and the like may be cited as the α -olefins and preferably propylene and butene-1. The content of the ethylene in the copolymer is within the range of 20 to 95 mole%, preferably 40 to 93 mole%, more preferably 65 to 90 mole% and most preferably 75 to 85 mole%.

Properties of the copolymer are a density of 0.91 g/cm³ or below and a Vicat softening point [ASTM D/1525 (value under a load of 1 kg)] of preferably 80°C or below, more preferably 70°C or below. In general, the copolymer is within the rubber-like region and includes substantially amorphous to partially crystalline copolymer of low degree, such as a crystallinity (measured by an x-ray diffractometry) of about 30% or less, if there is no difficulty in stretching. The copolymer of ethylene and the α -olefin used in this invention can be qualitatively determined even by infrared spectroscopic analysis. The copolymer is preferably a copolymer of ethylene and propylene or butene-1 especially preferably the former or a copolymer containing a compound having a small amount of a diene structure as a copolymer, and a thermoplastic elastomer which is a random copolymer, prepared by polymerization in the presence of a catalyst of a vanadium

...melt index of 0.1 to 10, preferably 0.2 to 6 is exemplified. Such a copolymer is supplied in the form of pellets without causing cold flow, as opposed to blocks in the case of ordinary unvulcanized rubber. The copolymer preferably has sufficient thermoplasticity so that, for example even a simple substance, can be extrusion processed into the form of a film.

The polymer (C) is now crystalline polypropylene and high-molecular weight crystalline polybutene-1 (hereinafter respectively abbreviated to IPP and PB-1) consisting of relatively rigid components having a relatively high degree of crystallinity. Such polymers preferably consist of relatively rigid polymers having a Vicat softening point of 100°C or above. IPP which is one of the polymer (C) refers to ordinary commercially available crystalline polypropylene having high isotacticity, and preferably includes propylene homopolymer, or copolymers of propylene and 7 mole% or less of α -olefins, such as ethylene, butene-1 or the like. Such respective copolymers may be optionally mixed.

The melt flow index is 0.1 to 30, preferably 0.5 to 20, more preferably 0.7 to 15. If the melt index is below the above-mentioned values, problems are caused in miscibility, optical characteristics and the like in processing. If the melt flow index is above the aforesaid values, problems are caused in extrusion stability

and stability of sealed parts in a large amount thereof used.

The polybutene-1 is crystalline polymer with a butene-1 content of 93 mole% or more and has a high molecular weight including copolymers with other monomers, is distinct from low-molecular weight liquid and waxy polymers. The melt index is preferably 0.2 to 10 for the same reasons as described above. Among them, IPP is preferably used as a principal component. The blend of IPP and PB-1 is preferably used. A rigid polymer, having moderate compatibility and dispersibility and fit for the object of this invention, if any, may be used in addition to the above-mentioned polymers.

The layer consisting of the specific blend composition (ABC) in the film of this invention is the most important layer for exhibiting strong cold stretching force and consists of the above-mentioned respective components. The combination and blended amounts are preferably expressed in weight ratios as follows: $0.90 \geq A/(A+B+C) \geq 0.20$, $0.50 \geq B/(A+B+C) \geq 0.05$ and $0.50 \geq C/(A+B+C) \geq 0.05$, and more preferably $0.80 \geq A/(A+B+C) \geq 0.30$, $0.40 \geq B/(A+B+C) \geq 0.10$ and $0.45 \geq C/(A+B+C) \geq 0.10$.

If the blended amounts of the soft component (B) are small, synergistic effects as a blend are hard to exhibit, and various characteristics are deteriorated. For example, strength, optical and low-temperature characteristics, flexibility, sealability, stretchability

and the like of films are deteriorated. If the amounts are too large, films have tendencies to too much softening, blocking, deteriorating heat resistance, sealing and optical characteristics and the like.

The component (C) has effects on synergistic improvement in tensile, and impact strength, heat resistance, extrusion moldability, modulus of elasticity, and heat sealing range with other components of the blend composition, particularly remarkable effects on heat and oil resistance, extrusion moldability, modulus of elasticity, heat sealing range, partial bearing of force for preventing zigzag whitening phenomena from occurring in the adjacent PVD layer in use, particularly in high shrinking and the like. The effects are as follows: If the blended amounts are small, for example processability of films and uneven section by flow characteristics in a die are deteriorated and the like and deficient in heat sealing range and heat resistance of the sealed parts. In particular, oil resistance of sealed parts are insufficient at high temperatures. Conversely, if the blended amounts are too large, low-temperature shrinkability, extrusion moldability, transparency, flexibility, impact resistance and the like are deteriorated and the like. Therefore, the blended amounts are preferably within the foresaid range. The component (A) consists of preferably specific ethylenic copolymer among those described above, and is sometimes a principal component in the blend

the above-mentioned three components (A), (B) and (C).

Among the three components, the aforementioned synergistic effects are hard to expect by blending only the components (A) with (B) usually because of poor miscibility and compatibility. Such disadvantages are remarkably improved by adding the component (B).

Reasons therefor are considered due to complicated synergistic effects, such as delicate interaction between characteristics resulting from a structure related to the copolymer with ethylene contained in the component (A) and other components, effects of crystal structure of the blend and dispersion state, treatment of the blend and the like.

As one of the greatest characteristics of this invention, it is important that the resin (B) selected from the aforesaid component (A) consists mainly of the above-mentioned linear-low-density polyethylene (LLDPE). Preferred ranges thereof are as follows. Melt index within the range of 0.2 to 10, more preferably 0.2 to 8, most preferably 0.2 to 6 and density within the range of 0.910 to 0.935 g/cm³, more preferably 0.910 to 0.925 g/cm³. The lower limit of the melt index is due to limits to extrudability into films. The upper limit is set, because values beyond the upper limit cause unstability to cold stretchability of the aforementioned principal component layer [consisting of the blend composition (ABC)] in utilization as the surface layer and deficiency in high-

temperature oil resistance of sealed parts and film strength or the like when formed into films. The lower limit of the density is due to the process for preparing the resin, and values beyond the upper limit tend to increase unstability to stretchability as in the case of the aforesaid upper limit of the melt index and deterioration in optical characteristics of cold drawn films, particularly those after shrinking and the like (for example, Haze value glossiness or the like). It is clear that such various factors are conversely remarkably improved within the above-mentioned range by synergistic effects with other layers without deteriorating the aforementioned processability and various characteristics and impairing various characteristics of the other layers, especially the ABC layer. In particular, various strength, sealing and high-temperature oil-resistance characteristics are markedly improved. The peak value of the crystal melting temperature (m_p) measured by the DSC method at a heating speed of $10^\circ\text{C}/\text{min}$) is preferably 110 to 125°C .

The linear low-density polyethylene which is the principal component may be mixed with other polymers for use so that the aforesaid various characteristics are not greatly damaged, and the limits thereof are about 50% by weight or less of other components to be mixed.

One object of combination of the above-mentioned layer construction is to synergistically improve various

characteristics, for example improve optical characteristics in the case of insufficient optical characteristics of only the (ABC) layer before and after shrinking without damaging properties as a whole. One of other objects is characterized in synergistic improvement, such as improvement of heat and oil resistance (especially at high temperatures) thereof in films or sealed parts, further cold-resistant strength and sealability (sealing range and sealing strength) and the like.

Further, it is important to use a vinylidene chloride copolymer (PVD) having a peak value of a crystal melting temperature (hereinafter abbreviated to mp) measured by using a differential scanning calorimeter (DSC method) within the range of 140 to 155°C as the PVD to be the core layer. The aforementioned various characteristics are synergistically improved by using the PVD within the range, the aforesaid adjacent layers and surface layers.

Other copolymerizable monomers, for example vinyl chloride, acrylonitrile, alkyl acrylates and others in an amount of 5 to 35% by weight are generally used in the PVD; however, they may be within the range without limitation on the monomers.

Since the simple copolymers are readily thermally decomposed, a small amount of stabilizers or plasticizers, as necessary, may be used according to a well-known method. The use of liquid plasticizers in a

large amount (for example, 7 to 12% by weight) is undesirable for improving stretchability or extrudability of the PVD. One reason therefor is as follows: Stretchability is hard to sufficiently carry out usually by a well-known method unless a large amount of plasticizers is used. In the process of this invention, devices are considered in selection of specific compositions and combination thereof even for layers other than the aforesaid PVD layer without requiring the use of the plasticizers. In this process, the aforementioned plasticizers used in a large amount sometimes destabilize stretchability and conversely cause puncture and the like. As another reason, disadvantages are cited as follows: The above-mentioned plasticizers used in a large amount greatly deteriorate oxygen-barrier performance of films, resulting in deficient high barrier performance. Attempts have been well known for providing a layer readily absorbing the aforesaid plasticizers, for example an EVA layer with a high vinyl acetate group content (VAc) of 28% by weight adjacent thereto, absorbing the plasticizers in aging for a long period and even slightly improving the barrier properties in order to prevent the disadvantages. In such processes, quality is unstable and different from that of this invention.

As a further reason, ply separation is extremely readily caused by using a large amount of the plasticizers, and various characteristics, such as heat

resistance, are deteriorated.

In the present invention, for the above-mentioned reasons, additives which are normally well-known to those skilled in the art and used, for example epoxidized soybean oil, dioctyl adipate or the like, as a stabilizer and acetyl tributyl citrate, dioctyl adipate or the like, as a plasticizer are preferably used in an extremely small amount of 3% by weight or less, preferably 2% by weight or less. If the amounts thereof used are small, the film is stable without substantially causing a change in barrier properties by migration of the plasticizer in a large amount without the aforementioned problems. In particular, the composition of this invention has oil resistance when used, and such phenomena are harder to see. In the process of this invention, since the respective layers, especially the PVD layer are sufficiently stretched by the specific resin layers (ABC layers), having sufficient stretching force and provided on both sides at a sufficient low temperature, strong cold stretchability is applied also to the PVD layer. PVD is believed to be stabilized by advancing crystallization together with orientation during the drawing. Furthermore, stretchability is surprisingly successful after sufficient progress of crystallization of the PVD in the aforesaid layer, for example even after 1 month. In this case, better results are sometimes obtained. Such results are synergistic effects with other layers of this invention,

and have influences as improved performance of cold resistance, various strength, lower-temperature shrinkage characteristics and optical characteristics before and after shrinking.

Moreover, preferably, non-migratory high-molecular plasticizers such as EVA, oligomers, rubber-like substances which do neither make the appearance opaque nor cause ply-separation can be used. In that case, the addition amount of said substances is preferably 1 to 15 wt.%, more preferably 2 to 10 wt.%.

PVD having a relatively low polymerization degree and good fluidity may be further used as a base. In this case, carbonization phenomena by decomposition tend to reduce and improve processing stability in extrusion and stretchability.

Such a kind of PVD is usually, particularly in an unstretched state, brittle and broken after stabilization even if quenched and processed into a film form, and has been considered undesirable. If the PVD is stretched at a higher temperature of about 84 to 105°C, as in the above-mentioned Japanese Patent Application KOKAI (Laid-Open) Nos. which are conventional examples, than this invention, poor films result. The PVD is of the type suitable for sufficiently cold stretchability to exhibit synergistic effects with specific other layers. Thus, unplasticized films free of a substantially low-molecular migratory plasticizer can be also obtained.

The combination of respective layers is required to provide the ABC layers on both sides adjacent to the PVD layer. The number of layers thereof is not particularly limited; however at least one layer, if necessary, more layers are required when expressed on one side.

In this invention, the (S) layer is provided on at least one surface layer on the outside to further synergistically make up insufficient points in the aforementioned layer. Other oil-resistant compositions may be used on other surface layers.

The aforesaid combination is expressed by abbreviations from the outside to inside as follows:

S/ABC/PVD/ABC, ABC/PVD/ABC, S/S/ABC/PVD/
ABC/S, S/ABC/ABC/PVD/ABC, S/ABC/ABC/PVD/
ABC, (S/ABC/ABC/PVD/ABC/ABC/S, EVA/ABC/PVD/
ABC/S, monomer resin/ABC/PVD/ABC/S and the like.

The thickness constitution ratio of the respective layers is as follows:

The PVD layer has a thickness of preferably 35 to 5% based on the total thickness, and the range thereof is 4 to 35 μ . The lower limits of ratio and thickness are levels required to maintain improved barrier characteristics and holding the quality. Oxygen barrier performance is 50 cc/m² day atm (23°C) or below, preferably 30 cc/m² day atm (23°C). This, however, does not apply to

uses requiring the oxygen barrier properties so much or conversely cases where presence of the barrier properties has a difficulty.

The upper limit of the above-mentioned thickness constitution ratio is a limit required to keep lower-temperature shrinkage characteristics or cold resistance, sealability, other various characteristics, particularly low-temperature characteristics.

The upper limit of the thickness thereof may be such that the upper limit of the aforesaid thickness constitution ratio is kept, and a too thick layer is practically unnecessary for practical use.

The (S) layer forming the surface layer has the sum of thickness at a ratio of preferably 5 to 40% based on the total thickness, and the range of the thickness is preferably 2 to 25 μ , more preferably 3 to 20 μ . The lower limit thereof is a thickness required to provide a role as the surface layer.

The upper limit is set, since function of the ABC layer is deteriorated if the thickness is too great. If the resin has low stretchability as the surface layer under the conditions of this invention, the ratio thereof is preferably low. The blend resin layer consisting of the ABC constituting the principal component has a thickness ratio of 25 to 90% except the surface layer in 65 to 95% exclusive of the PVD layer in principle.

The whole thickness is normally 30 to 100 μ ,

preferably 35 to 80 μ in uses for directly packaging relatively large raw meat, processed meat or the like. This, however, does not apply to cases of uses particularly as thin-walled barrier packages and the like. Even a film having a thickness of 5 to 30 μ is found to be sufficiently usable. This is based on synergistic effects, such as strength characteristics due to characteristic layer constitution, high strength, high barrier physical properties and the like obtained by highly stretching practically unplasticized PVD.

Reasons for providing the thickness constitution (μ) and ratio (%) of the aforesaid respective layers are as follows:

The ABC layer defined above must be initially provided on the adjacent layer in the case where the peak of mp in DSC of the PVD layer is present within the range of 140 to 155°C. If simple EVA layers (VAc: 10.2 mole%, MI: 4) having a thickness of 3 μ are provided adjacent to both sides to form adhesive layers, whitening phenomena already occur even at a shrinkage factor of 30% (average of longitudinal and transverse directions) by paying attention to optical characteristics after shrinking. When the film was sliced to observe photomicrographs of sections, zigzag flexes (hereinafter referred to as zigzag whitening) of the PVD layer were observed to find that abnormal phenomena definitely occurred. Such films are whitish, and contents become dim and hard to see, not only

markedly deteriorating merchandise value but also resulting in ply separation and deterioration in strength of sealed parts. The phenomena were hardly noted by shrinking at 85°C in all the cases where a PVD layer having an mp within the above-mentioned range is used to constitute a specific ABC layer and all the layers are stretched at a sufficiently low temperature under the conditions of this invention. If PVD having an mp over the upper limit of 155°C is used, a tendency of zigzag whitening to occur is observed even if the ABC layer is provided. The cold resistance has also a tendency to deteriorate. As described above, this tendency is noted even if a large amount of a plasticizer (6% by weight or more) is used in the PVD layer.

The PVD layer having an mp below the aforesaid lower limit has a tendency to deteriorate stretching stability, barrier properties, heat resistance and the like.

As mentioned above, the film of this invention is capable of exhibiting unprecedented improved physical properties by synergistic effects of the specific layer of a specified PVD copolymer with layers on both sides thereof.

As one of the greatest characteristics indicating lower-temperature shrinkability thereof, the film of this invention has heat shrinkage factor values of at least 15 and 25%, preferably 20 and 30%, more preferably

22 and 35% at the respective temperatures of 70 and 80 °C. The values are averages of shrinkage factors in the longitudinal and transverse directions measured according to a method for dipping the film in given hot water for 4 seconds.

A higher value means high lower-temperature shrinkage performance, and a smaller difference between both means that good shrink packaging can be carried out with small temperature dependence in shrinking. This value is expressed by a value providing the maximum shrinkage factor difference at a temperature difference of 10 °C within a practical range (range with a shrinkage factor of 20 to 50%), in short, the film of this invention has a value $[(\Delta \text{ shrinkage factor } (\%) / \Delta 10 (^\circ\text{C}))]$ of 1.5 or below, preferably 1.4 or below, more preferably 1.3 or below expressed in terms of shrinkage gradient $[\Delta S / \Delta T]$. In comparison with this, commercially available barrier shrink films (a) and (b) described below have a shrinkage gradient of 2.8 and 1.9.

The shrinkage stress value has the peak value within a relatively lower temperature range of 50 to 80 °C, and the maximum value thereof is at least 100 g/mm^2 , preferably 125 g/mm^2 , more preferably 140 g/mm^2 . The shrinkage stress, together with the above-mentioned shrinkage factor, exhibits characteristics of providing sufficiently tight and firm packages.

A lower shrinkage temperature and high stress

value thereof at a lower temperature provide great advantages in that the film which is a packaging material can be packaged without disadvantages, i.e. deterioration of films (because of melting and disorienting), and deteriorating various characteristics (strength, strength of sealed parts, optical characteristics and the like) and further remarkable effects on prevention of deterioration in quality by producing broth (drip) and by boiling in case a material to be packaged is raw meat or the like.

Well balanced both characteristics provide excellent creaseless packages.

One of other characteristics is improved cold-resistant impact strength, and the film has a falling weight impact strength of 150 kg·cm or above, preferably 170 kg·cm or above measured at 5°C according to the ASTM D1709-75. Commercially available products (a) and (b) respectively have values of 130 kg·cm and 145 kg·cm: but some may have a value of 230 kg·cm in Example described below. In the values, the film of this invention is excellent due to sufficient cold stretching of all the layers and impartment of high orientation. It is found that the PVD layer is most inferior in cold resistance and the film is broken therefrom to propagate the breakage and cause burst. The film of this invention is considered at a high level due to high orientation by synergistic effects of the whole layer. Since the strength is too high, measurement is hard by an ordinary method, and the following

method is considered: That is, even when a missile, having a groove part with notched edges and capable of imparting film notch effect is used as a falling weight in order to clearly show a significant difference in the test, the film, for example film of Run No. 1 has a falling weight impact strength of 67 kg-cm at -30°C. In comparison with this, the aforesaid commercially available films (a) and (b) have a falling weight impact strength of 25 and 27 kg-cm. This film is found to have excellent strength.

Referring to Fig. 2, this relation is clearer.

As one of the greatest features, the film of this invention is characterized by lower-temperature shrinkability and improved high-temperature heat-oil resistance. The method for measurement is to prepare a sealed film, i.e. a sample 10 cm in length with the central part 60 μ in thickness and 15 cm in width sealed in the form of folded palms, sufficiently apply lard to both sides of the central sealed parts, hang a given weight from the lower sample piece, dip the sealed part in a water bath at a given temperature, record the time required for high-temperature oil (lard) to attack and break the sealed part. A method for grasping a load kept unbroken for 60 seconds or more in relation with temperature is adopted. According to this method, the film of this invention is found to have a strength of 100 g/15 mm width or more, preferably 150 g/15 mm width or more even

at a temperature of 95°C, and especially improved as compared with a value of 3 and 20 g/5 mm width of commercially available products (a) and (b) poor in oil resistance. This is an important factor which means that packaging can be safely carried out while preventing occurrence of drip (broth) due to tight shrinkage in vacuum packaging oily food, particularly oily processed meat, such as ham, bacon, sausage or the like, then shrinking the film and improving appearance or simultaneously sterilizing the food or the like. This is evidence indicating that the film of this invention is especially improved in such various characteristics. Referring to Fig. 3, advantageousness of this invention is clearer.

Excellent optical characteristics before and after shrinking may be cited as one of the greatest features of this invention. This is excellent in not only optical characteristics in the initial shrinking but also high shrinkage factor after shrinking. In short, for example the rate of change in Haze value is generally small for shrinkage factor. This value is 15% or less, preferably 10% or less expressed in terms of Haze value after 10% shrinkage. More important is practically a value after high shrinking. Such parts are often present in edge, free, clip, sealed parts, crease parts or the like in actual packaging, naturally causing parts of a high shrinkage factor.

If a material to be packaged is small for the size of a packaging film—this case is often found in practical use—there are disadvantages in that the above-mentioned whitening phenomena occur in ordinary commercially available films to remarkably damage appearance in such cases. The commercially available films (a) and (b) have a Haze value of 40 and 80%, and reach 80 to 90% in 60% shrinkage and are wholly whitened. The value for the film of this invention is expressed by 50% shrinkage and is preferably 40% or less, more preferably 35% or less.

Thus, in this invention, the level of unconventional improved optical characteristics can be attained by synergistic effects of the whole layers.

As a result of analysis tried for the whitening phenomena, it is clarified that the surface layer other than the PVD layer is roughened from the beginning, roughened during shrinking or the like and further the principal cause thereof is phenomena of transfer of generated zigzag flexes (zigzag whitening phenomena) of the above-mentioned PVD layer, diffused reflection at the interface between layers and peeling of the interface.

Reasons therefor are as follows: Such phenomena are found to readily occur with the shrinking temperature of the film shifted to a higher side; steeper shrinkage gradient, lower softening point and *mp* per se regardless of thick or thin polymer layer constituting the adjacent

layers, simple polymer, higher (DSC) \bar{m} of the PVD layer, lower orientation degree (lower stretching degree, higher stretching temperature, factors due to resin or the like), easier occurrence of peeling phenomena between the PVD layer and the adjacent layer at high temperatures. It is a matter of course that, besides the above-mentioned optical characteristics, sealing strength, oil-resistant strength, ply separation phenomena and various strengths are markedly reduced if the phenomena occur.

On closer examination, it was clear that the commercially available film (a) caused zigzag whitening phenomena at a shrinkage factor of 43% at 90°C, and the commercially available film (b) caused the whitening phenomena rapidly at 85°C after a shrinkage factor of 40%. Microscopic examination showed appearance of the phenomena here and there even before that. In comparison, no such phenomenon occurred in Example Run No. 1 of the film of this invention. All the afore-mentioned Haze values are expressed in terms of 60 μ . If the film is thicker than 50 μ , or, if necessary, colored, fabricated, embossed or laminated, the same does not apply to the case.

The film of this invention has a high tensile strength (measured by the ASTM D882-67) and normally a breaking strength of 5 kg/mm² or above, and preferably a strength of 7 kg/mm² or above.

As one use, the film of this invention is employed by sealing in the form of a bag under severe

conditions even in general usage, for example vacuum packaging in a state of sticking fats and oils and shrinking at high temperatures or the like. Thus, the film is required to have improved oil resistance.

The film of this invention is characterized by excellent binding properties (sealability by clip) in vacuum packaging and slight vacuum return by pinholes in binding, and this is a result of the aforesaid synergistic effects.

One example of processes for preparing a film consisting of the polymers in combination of this invention is detailed hereinafter; however, this invention is not limited thereto.

In this invention, the above-mentioned polymer composition, as necessary, thermoplasticized by respective separated extruders, melted and normally extruded through a multilayered die to provide a raw film, and, as necessary, a sufficiently uniform tubular raw film is preferably formed by quenching and solidifying a just extruded film to 20°C or below with a liquid refrigerant optionally according to other methods.

The resulting at least 4-layer raw film containing the aforementioned ABC layer, PVD layer and S layer is heated at 100°C, or below preferably 90°C or below, more preferably 85°C or below, most preferably a temperature without melting crystal components which are principal components in the ABC and S layers and damaging the

quenched properties and then inflated into a bubble form at a temperature of 90°C or below, preferably 35 to 80°C, more preferably 35 to 70°C and most preferably at a temperature lower than the melting point of the crystal components which are principal components of respective compositions of the above-mentioned layers, most preferably below the Vicat softening points of the original polymers which are principal components or blend under a sufficient internal pressure, for example 100 to 3000 mm H₂O. Thereby a desired film is only obtained in good condition. The optimum area stretch ratio at this time varies with the respective compositions, layer constitutions, temperatures or the like, but generally 5 to 20 times, preferably 7 to 15 times, and the stretch ratio in the transverse direction carried out in a preferred case is generally 2 to 6 times, preferably 2 to 4 times. It is particularly important that conditions for providing sufficient cold stretching with prevented puncture are the respective combinations and layer combinations within the aforesaid range at this time, and preparation of a sufficient uniform is important at the same time.

The stretching degree is as follows:

After determining the stretching ratio in the longitudinal direction by the speed ratio of feed nip rolls and take-off nip rolls, the best method for most stably stretching is to seal air in a bubble, stretch the bubble to the vicinity of the stretching end point (just

before whitening of the ABC layer) of the bubble so that the inflation in the transverse direction is stopped and directly deflate the bubble at the largest-diameter part by a roll type deflator. The raw film bubble is favorably a large size, such as a diameter of about 30 mm or more, preferably a diameter of 50 mm or more so far as an apparatus permits in relation between internal pressure and diameter. Although stretching is preferably carried out while sufficiently cold so far as bubble stability permits concerning physical properties of the resulting film, the stretching degree may be actually determined by the composition in balance with stability (not to puncture).

The whole layer is uniformly, stably and highly stretched by characteristics of this process with slight transfer of heat and further synergistic effects on high stretching of the respective many layers to provide a film having the above-mentioned characteristics. In comparison, such things are not found in an ordinary method for heating above the melting point, and stretching temperature should be further conversely increased. Orientation is increasingly harder to apply, and strength often tends to lower.

This may be the same with a temperature of melting point ± 5 to 10°C , and not only favorable results of optical characteristics are not obtained, but also high characteristics may be hardly imparted by the blend com-

position, since the raw film is particularly just under brittle temperature condition and punctured. In particular, if different kinds of resins are combined in many layers, respective stretching optimum temperatures of the resins are different, and there are many combinations incapable of stretching the whole layers. After all, impartment of orientation by driving of any layer is often sacrificed.

Successful stretching herein described has not hitherto been achieved in the whole layers at a cryogenic temperature, for example 47°C , as in the following Examples of this invention. The stretching can only be attained by synergistic effects of using, for example a multilayered tube containing the specific aforesaid copolymer layer and uniform quenched raw film, satisfying conditions, such as a specific stretching method and the like.

Further, the heating temperature herein is the maximum temperature for the raw film before stretching. The stretching temperature herein described is a temperature of parts where the stretching is started. The temperature is further reduced to a region where the stretching ends by cooling. In the region where the stretching ends (region where the bubble reaches the maximum diameter), sufficient cooling is carried out to provide at least 40°C or below, preferably 30°C or below, more preferably 25°C or below. Therefore, the temperature difference between the stretching

starting part and ending part is at least 5°C or more, preferably 10°C or more, more preferably 15°C or more. Such temperatures are obtained by measuring the bubble surface using a contact type thermometer. For example, in the case of Run No. 8, the temperature of the stretching starting part was 54°C, and the temperature was 50°C and 39°C respectively at places of 1/3 and 2/3 from the raw film in an inflating region of the bubble maximum diameter and the raw film. The temperature in the end region was 25°C. As described above, the process of this invention is found to be an unprecedented cold stretching method.

This invention is illustrated by citing Examples which follow.

Example 1

(a₁) Ethylene vinyl acetate copolymer with a vinyl acetate (VAc) content of 5.5 mole%, a melt index (MI) of 1.0, a crystal melting point (mp) of 88°C and a Vicat softening point (Vsp) of 72°C in an amount of 60 parts by weight was blended with (b₁) 20 parts by weight of a thermoplastic ethylene- α -olefin copolymer elastomer (with an MI of 0.45, a density of 0.88 g/cm³ and a Vsp of 40°C or below prepared by randomly copolymerizing 15 mole% of propylene as an α -olefin with 2% by weight of ethylidene norbornene) and (c₁) 20 parts by weight of crystalline polypropylene [with a melt flow rate (MFR) of 7.0, a density of 0.89 g/cm³, and a Vsp of 143°C] prepared by

copolymerizing 4% by weight of ethylene) and used for the blend composition (Vicat softening point: 67°C) ABC_{111} layer. LLDPE (with an MI of 2.0, a density of 0.915 g/cm³, an mp of 116°C having a peak at 120°C and a Vsp of 98°C prepared by copolymerizing 3.5 mole% of octene-1 as the α -olefin) was used as the resin (S_1) for the surface layer. Furthermore, 100 parts by weight of a vinylidene chloride copolymer (with a DSC peak temperature mp of 145°C prepared by copolymerizing vinyl chloride), was blended with 2 parts by weight of EVA with a VAc content of 40% by weight, 1 part by weight of epoxidized soybean oil and 0.5 part by weight of acetyl tributyl citrate to provide a PVD composition (PVD_1), which was used as a resin for the PVD layer. The above-mentioned blend compositions were respectively and separately thermoplasticized by three extruders, fused in a three-kind five-layer die, extruded at an average resin temperature of 190°C and quenched with cold water at about 8°C at a point of 5 cm from the tip of the aforementioned die to prepare tubular raw films having the respective layers having a folding width of 120 mm and a thickness of 650 μ with uniform thickness accuracy.

The layer constitution was adjusted to provide the raw films of $S_1 = 60 \mu / ABC_{111} = 130 \mu / PVD_1 = 100 \mu / ABC_{111} = 300 \mu / S_1 = 60 \mu$ from the outside of the tube.

Such raw films were passed between 2 parts of feed nip rolls and take-off nip rolls at a higher speed

than the above-mentioned rolls and heated at 47°C with hot air therebetween, and air was directly introduced into the interior to continuously inflate the films and stably stretched the films at almost 3.1 times in the longitudinal direction and 3.5 times in the transverse direction. The stretching end region was cooled with airing with blowing cold air at 15°C, folded in by a roll type deflator, taken off by nip rolls and directly wound to provide given films.

Furthermore, stretching was very stably performed by using a rectifying contact guide for the purpose of substantially isolating the heating part and the stretching starting part in order to smoothly carry out cold high stretching while discontinuously contacting and removing a fluid accompanying the film surface during stretching and laminar films thereof in the circumferential direction and then, if necessary, similarly carrying out the contact guide for the bubble part during stretching, preparing a substantially independent a temperature controlled air chamber, stretching and drawing the film, thereby providing a stepwise temperature controlled air chamber on the film and performing zone control.

The resulting films were tubular films having the total thickness of 60 μ of 5.5 μ /12 μ /9.2 μ /27.8 μ /5.5 μ in the order of the aforesaid raw films.

The respective thicknesses were then changed in the similar layer constitution to afford films shown in

Table 1-Run-2- (the outermost layer was counted as the first layer hereinafter).

Table 1

Run No.		2	3	4	5	6
Thickness constitution of product						
First layer	(μ)	3	5	6	6	-
Second layer	(μ)	4	10	15	15	12
Third layer	(μ)	6	8	10	15	10
Fourth layer	(μ)	14	12	31	29	33
Fifth layer	(μ)	3	5	8	15	5
Total thickness (μ)		30	50	70	80	60

Comparative Run No. 1 is a comparative example, and a raw film having the total thickness of 650 μ with the raw film constitution ratio of 180 μ /30 μ /110 μ /30 μ /300 μ expressed in the same manner successively from the first layer. Stretching was similarly tried, resulting in puncture in the initial stage of introducing air into the tube and blowing up the film. Thus, the film could not be entirely stretched to afford products.

Table 2 shows values of various characteristics of the resulting films and two kinds of commercially available films which were comparative examples.

Table 2

Characteristics		Run No.				
	Unit	1	2	3	4	5
After 10% shrinkage	%	4.0	3.5	4.0	4.2	5.0
After 50% shrinkage		19	18	20	22	23
Zigzag whitening phenomenon *1		◎	◎	◎	◎	◎
Shrinkage factor at 70°C	1/°C ² g/min °C	26	27	29	25	23
Shrinkage factor at 80°C		40	41	40	39	38
Shrinkage gradient		1.1	1.0	1.1	1.2	1.1
Shrinkage stress		190	100	215	200	100
Position of shrinkage stress peak	°C	60	72	69	67	68
Breaking strength	kg/mm ²	13	12	13	11	14
Breaking elongation		260	250	265	230	245
Falling weight impact strength *2 at -30°C (expressed in terms of 60 μ)	kg·cm	67	75	70	75	85
Oxygen barrier characteristics (23°C)	cc/m ² ·day·atm	25	40	37	24	15
Oil resistance of sealed part (95°C)	g	215	190	210	220	250

- cont'd -

Table 2 (cont'd)

	Comparative	
	(a)	(b)
4.5 27 ⊙	5.1 40 X	11.0 80 X
30 42 1.2 178 66	3 13 2.8 85 95	10 24 2.2 120 85
11 250 70 20 200	6.5 240 25 48 3	6.0 230 27 43 20

* 1 zigzag whitening phenomenon

- ⊙ : No occurrence at all
- : Partial occurrence at a high shrinkage factor (50% or above)
- Δ : Occurrence on the whole surface at a high shrinkage factor (50% or above)
- X : Occurrence on the whole surface at a medium shrinkage factor (about 40%)

* 2 Use of an edged special missile

(with 0 grooves having a radius of 2 mm formed in the direction of the tip in hemispherical missile)

Measurement was made by cutting shrunk samples of size 10 cm x 10 cm dipped in hot water at 50°C for 5 seconds and observing the cross section.

Examination of the barrier properties when aged at 25 °C for 1 month just after preparing the film of Run No. 1 confirmed that the stability was good with hardly any change.

The sample of the commercially available Comparative example (a) was a barrier shrink pack for packaging raw meat having the thickness constitution of 16 μ /10 μ /34 μ with the total thickness of 60 μ and the layer constitution of EVA/PVD/crosslinked EVA. The cross-linked layer had a content of gel insoluble in boiling. Xylene of 50% by weight, and the content of VAc in EVA was 9.5% by weight.

The sample of the commercially available Comparative example (b) was a barrier shrink pack for packaging raw meat having the thickness constitution of 15 μ /1 μ /8 μ /1 μ /35 μ with the total thickness of 60 μ and the layer constitution of EVA/EVA with a high VAc content/PVD/VAc with a high VAc content/ionomer resin.

All the films obtained as described above are films having improved optical characteristics, lower-temperature shrinkability and various strengths, and films of Run No. 1, Comparative Run Nos. (a) and (b) packaging 10 kg of raw meat were dipped in hot water under respective conditions for 5 seconds to carry out shrink packaging. Creases were smoothed with hot water at 75 to 80 °C to finish tight packages by using the film of Run No. 1, and the film of Comparative Run No. (a) was finished

within a narrow range of 93 to 95°C with a partially occurring whitening phenomenon. Although the film of Comparative Run No. (b) was finished relatively tight at 85 to 90°C, the whitening phenomenon also occurred in partially much shrunk area. Appearance of the packages was best for Run No. 1, Comparative Run Nos. (a) and (b) in the decreasing order. When such packages were cooled to 0°C and dropped from a height of 1 m, the film of Run No. 1 did not break the bag even by dropping 10 times. The film of Comparative Run No. (a) broke the bag by dropping once, but that of Comparative Run No. (b) broke the bag by dropping three times. Observation after preservation at 0 to 5°C for 1 month showed that the film of Run No. 1 had both excellent appearance and quality with the least occurrence of broth (drip). This was considered as effects that shrinking could be carried out at lower temperature without leaving creases and the like on the surface. The return of color was best on opening the seal. When commercial ham was halved into blocks weighing about 1.3 kg and vacuum packaged (marginal dimension of about 15%) tight with the respective films and dipped in hot water at 98°C floating lard, the film of Comparative Run No. (a) peeled the surface layer part in about 3 seconds, and the sealed part was instantaneously broken and torn. The surface layer part of Comparative Run No. (b) was dissolved and peeled in about 10 seconds, and the sealed part was broken. Such a phenomenon did not

occur in the film of Run No. 1 of this invention even after 5 minutes to prove that both oil resistance and shrinkability were improved. Respective films were cut to a size of 10 cm x 10 cm and dipped in lard at 60°C, and lard was permeated from the cuts of the films of Comparative Run Nos. (a) and (b) after 40 minutes to cause a ply separation phenomenon. The phenomenon did not occur in the films of Run Nos. 1 to 6. This is because oil was permeated from layers deficient in oil resistance at the cuts and interlaminar bonding to cause a peeling phenomenon.

Example 2

Respective raw films were prepared in the same manner as in Example 1 by using a four-kind five-layer die, if necessary, to provide films having the layer constitutions shown in Table 3. Stretching was respectively carried out at temperatures of 55, 59, 60, 56 and 62°C in Run Nos. 7 to 11, and 58, 61, 60, 67 and 42°C in Comparative Run Nos. 2 to 6. Only the thicknesses of the raw films were shown for Comparative Run Nos. 2 to 5 in parentheses in the table.

Table 3

Run No. Thickness Constitution	7	8	9	10	11
First layer (μ)	S ₂ 6	S ₃ 5	S ₄ 4	S ₁₀ 6	S ₉ 5
Second layer (μ)	ABC _{112+C₁} 10	ABC ₁₁₁₋₁ 13	ABC ₁₁₂ 13	ABC ₂₁₁ 10	ABC _{112+C₁} 15
Third layer (μ)	PVD ₁ 9	PVD ₂ 10	PVD ₂ 10	PVD ₂ 11	PVD ₂ 9
Fourth layer (μ)	ADC _{112+C₁} 29	ADC _{211+S₂} 20	ADC ₁₁₂ 30	ABC ₂₁₁ 27	ABC _{112+C₁} 22
Fifth layer (μ)	S ₂ 6	S ₃ 6	S ₄ 4	S ₁₀ 10	S ₁ 0
Total thickness (μ)	60	62	61	64	59

- cont'd -

Table 3 (cont.)

Comparative 2	Comparative 3	Comparative 4	Comparative 5	Comparative 6
S ₅ (60)	S ₆ (60)	S ₇ (60)	S ₈ (55)	S ₉ 6
ABC ₁₁₁ (150)	ABC ₁₁₁ (100)	ABC ₂₁₁ (120)	ABC _{112+C2} (150)	ABC ₁₁₂ 15
PVD ₂ (65)	PVD ₂ (70)	PVD ₂ (60)	PVD ₂ (60)	PVD ₂ 10
ABC ₁₁₁ (265)	ABC ₁₁₁ (350)	ABC ₂₁₁ (300)	ABC _{112+C2} (250)	ABC ₁₁₂ 23
S ₅ (60)	S ₆ (70)	S ₇ (60)	S ₈ (65)	S ₉ 6
(600)	(650)	(600)	(500)	60

Kinds of resins

- o S₂-linear-low-density polyethylene (MI: 1.0, density: 0.917 g/cm³, mp: 118°C, Vsp: 102°C)
- o S₃-linear-low-density polyethylene (MI: 5.5, density: 0.920 g/cm³, mp: having the peak at 118 122°C; Vsp: 99°C)
- o S₄-linear-low-density polyethylene (MI: 2.0, density: 0.924 g/cm³, mp: 121°C, Vsp: 112°C)
- o S₅-linear-low-density polyethylene (MI: 25, density: 0.919 g/cm³, mp: 121°C, Vsp: 95°C)
- o S₆-linear-low-density polyethylene (MI: 6, density: 0.935 g/cm³, mp: 124°C, Vsp: 113°C)
- o S₇-high-pressure process-low-density polyethylene (conventional LDPE undesignated as linear) (MI: 2.0, density: 0.919 g/cm³, mp: 105°C)
- o S₈-medium, low-pressure-high-density polyethylene (ordinary HDPE) (MI: 1.0, density: 0.950 g/cm³, mp: 132°C)
- o ABC₂₁₁-blend of (a₂) 65 wt.% of EVA (VAc: 4.1 mole%, MI: 1.0, mp: 95°C, Vicat: 78°) with (b₁) 20 wt.% of ethylene-α-olefin elastomer (as described above) and (C₁) 15 wt.% of IPP with a Vsp of 64°C
- o ABC₁₁₁₋₁-blend of (a₁) 55 wt.% of EVA with (b₁) 15 wt.% of ethylene-α-olefin elastomer and (C₁) 30 wt.% of IPP

with a Vsp of 70°C

o $ABC_{211} + S_2$ - 70 wt.% of the above-mentioned ABC_{211} with 30 wt.% of the following S_2 with a Vsp of 70°C

o ABC_{112} -blend of (a_1) 45 wt.% of EVA with (b_1) 15 wt.% of ethylene- α -olefin elastomer and (C_2) 40 wt.% of crystalline polybutene-1 (MI: 2.0, density: 0.910 g/cm³, Vsp: 105°C, modified with 5 mole% of ethylene, mp: 110°C)

with a Vsp of 84°C

o $ABC_{112} + C_1$ -blend of (a_1) 45 wt.% of EVA with (b_1) 20 wt.% of ethylene- α -olefin elastomer (C_2) 15 wt.% of crystalline polybutene-1 and (C_1) 20 wt.% of IPP

with a Vsp of 83°C

o $S_9 = (a_2)$ EVA (as described above)

o PVD₂-composition prepared by adding 1 part by weight of epoxidized soybean oil, 1 part by weight of acetyl tributyl citrate and 2 wt.% of EVA with a VAc content of 40 wt.% to 100 parts by weight of a vinylidene chloride copolymer (copolymer of vinylidene chloride having a DSC peak temperature of 142°C)

o S_{10} -blend of 70 wt.% of (S_1) with 30 wt.% of (a_2)

Characteristics of the resulting films are shown in Table 4.

Stable cold stretching of Run Nos. 7 to 11 could be attained; however, samples of Comparative Run No. 2 were readily punctured in bubbling up of the initial stretching,

and stable stretching could not be attained. Even when stretching temperature was reduced to 40°C or increased to 95°C, streaks tended to longitudinally occur, and sufficient stretching could not be carried out.

Samples of Comparative Run No. 3 have a tendency similar to that of Comparative Run No. 2 and were harder to draw and readily puncture.

Samples of Comparative Run No. 4 seemed to bubble up just before stretching though unstable, but tended to puncture, leaving streaky uneven thickness. This tendency resulted in whole whitening and opacity by increasing temperature in the same manner as above, and puncture tended to occur. Sufficient stretching could not be carried out.

Samples of Comparative Run No. 5 were instantly punctured when air was introduced into the bubble, and stretching could not be conducted at a temperature between 30 to 95°C.

Stretching of samples of Comparative Run No. 6 could be stably and continuously carried on at a sufficiently low temperature of 42°C.

Characteristics		Run No.	7	8	9	10	11	Com- para- tive
General properties	After 10% shrinkage	Units	5.0	5.0	7.5	9.0	4.5	6
	After 50% shrinkage		30	33	35	38	28	3.0
	Zigzag whitening phenomenon		⊙	⊙	⊙	⊙	⊙	24
	Shrinkage factor at 70°C		25	23	23	27	25	⊙
Thermal stability	Shrinkage factor at 80°C		40	39	37	42	40	30
	Shrinkage gradient	1/°C ²	1.0	1.0	1.0	1.1	1.0	44
	Shrinkage stress	g/mm	195	200	210	192	220	1.1
	Position of shrinkage stress peak		70	73	75	72	71	190
Tensile properties	Breaking strength	kg/mm ²	13	12	11	11	12	70
	Breaking elongation		250	260	230	210	240	10
Falling weight impact strength *1 at -30°C (expressed in terms of 60 μ)		kg·cm	74	70	72	69	80	245
Oxygen barrier characteristics (23°C)		cc/m ² ·day·atm	25	29	30	28	33	65
Oil resistance of sealed part (95°C)		gr	210	220	190	250	230	30
								15

*1 Measured by the method similar to that in Tabale 2.

Example 3

Stretching was carried out by the same method, layer combination and conditions as in Example 1, except that copolymers having respective mp values of 141, 149 and 154°C expressed in terms of DSC peaks in the vinylidene chloride copolymer layers were taken as Run Nos. 12, 13 and 14 and those having mp values of 135 and 160°C were designated as Comparative Run Nos. 7 and 8. The samples of the copolymers having the mp of 141, 149 and 154°C could be successfully and stably stretched, but the sample of the copolymer having the mp of 135°C was unstable without stopping elongation and tended to puncture in stretching. The sample of the copolymer having the mp of 160°C was hard to sufficiently and completely stretch, brittle and tended to puncture. Partial samples of Comparative Run No. 8 were simultaneously evaluated to find that optical characteristics of Run Nos. 12, 13 and 14 were much the same as those of Run No. 1. Samples of Comparative Run No. 8, however, caused marked zigzag phenomena even with a low shrinkage factor. The sample of Comparative Run No. 8 had insufficient shrinkage factors of 10% at 70°C and 15% at 80°C, a low stress of 60 g/cm², a breaking strength of 4.3 kg/cm² and a falling weight impact strength of 40 kg cm at a low level using the above-mentioned edged missile at -30°C though heat shrinkage characteristics of others were good. On the other hand, the others exhibited excellent values. This

was considered due to the PVD layer.

The oxygen barrier performances of Run Nos. 12, 13 and 14 and Comparative Run No. 8 were respectively 43, 19, 12 and 8 cc/m².day.atm in order.

Example 4

Stretching was carried out by the same method and layer constitution by using vinylidene chloride/vinyl chloride copolymer having the peak of mp 150°C and changing additives of the PVD layers to provide films. In the case of Comparative Run No. 11, the three-layer films having the first and third layers consisting of EVA with a VAc content of 28% by weight were used, and three-layer films having the first and third layers consisting of EVA with a VAc content of 18% by weight were used in Comparative Run No. 12 with the respective thickness ratios of 20 μ/10 μ/30 μ.

Table 5

Additive	Run No.	15	16	17	18	19	20
High polymer plasticizer EVA (VAc 40%)	4	2	2	2	2	0	2
Acetyl tributyl citrate	0	0	1	0	0	1	1
Dibutyl sebacate	0	0	0	1	1	0	1
Stabilizer epoxidized soybean oil	1	1	0.5	0.5	0.5	0.5	0.5
Total amount of liquid additive	1	1	1.5	1.5	1.5	1.5	2.5

- cont'd -

Table 5 (Cont'd)

Comparative	Comparative	Comparative	Comparative	Comparative
10	11	12	13	14
0	0	0	0	0
8	0	0	0	0
0	0	0	0	0
8	8	8	8	8

(Units are parts by weight based on 100 parts by weight of the PVN copolymer.)

No phenomenon particularly inferior to those of Run No. 1 in Example 1 was found in Run Nos. 15 to 20, and characteristic values were at good levels with little difference. In contrast to this, samples of Comparative Run Nos. 9 and 10 were readily punctured, but stretching could be relatively smoothly conducted. Raw films of Comparative Run Nos. 11 and 12 were especially easily blocked and unstable, and good stretching could not be practiced. Since films of Comparative Run Nos. 9 and 10 used a special blend composition having oil resistance in the layers adjacent to the PVDC layer, ply separation tended to occur in the lapse of a while after stretching. Films of Comparative Run Nos. 11 and 12 were sticky and readily blocked without stiffness. Changes of barrier properties with time were examined to obtain the following results: Films of Run Nos. 15 to 20 hardly changed at room temperature with time even after 15 days and had a value of about $23 \text{ cc/m}^2 \cdot \text{day} \cdot \text{atm}$ (23°C). Films of Comparative Run Nos. 9 and 10 showed a value of 150 cc immediately after the stretching and resulted in 120 cc. Films of Comparative Run Nos. 11 and 12 exhibited a value of 145 cc just after the stretching and reduced to 90 and 95 cc both at low levels. Zigzag whitening occurred in all the films of Comparative Run Nos. 9, 10, 11 and 12 by shrinking with time, especially markedly in Comparative Run Nos. 11 and 12. At the time of shrinking, those of Comparative Run Nos. 11 and 12 were softened and became

sticky and hard to be practicable.

Shrinkage stresses of Comparative Run Nos. 11 and 12 were 40 and 50 g/mm², and oil resistance test of sealed parts showed a state of instantly peeling even under a load of 5 g.

Comparative example 1

Raw films were obtained in the same manner as in Examples, and stretching was carried out by adjusting layer constitution so as to provide composition and layer constitution as shown in the following Table 6.

Table 6

Run No.	Comparative	Composition
11	11	11
12	12	12
13	13	13
14	14	14
15	15	15
16	16	16
17	17	17
18	18	18
19	19	19
20	20	20
21	21	21
22	22	22
23	23	23
24	24	24
25	25	25
26	26	26
27	27	27
28	28	28
29	29	29
30	30	30
31	31	31
32	32	32
33	33	33
34	34	34
35	35	35
36	36	36
37	37	37
38	38	38
39	39	39
40	40	40
41	41	41
42	42	42
43	43	43
44	44	44
45	45	45
46	46	46
47	47	47
48	48	48
49	49	49
50	50	50
51	51	51
52	52	52
53	53	53
54	54	54
55	55	55
56	56	56
57	57	57
58	58	58
59	59	59
60	60	60
61	61	61
62	62	62
63	63	63
64	64	64
65	65	65
66	66	66
67	67	67
68	68	68
69	69	69
70	70	70
71	71	71
72	72	72
73	73	73
74	74	74
75	75	75
76	76	76
77	77	77
78	78	78
79	79	79
80	80	80
81	81	81
82	82	82
83	83	83
84	84	84
85	85	85
86	86	86
87	87	87
88	88	88
89	89	89
90	90	90
91	91	91
92	92	92
93	93	93
94	94	94
95	95	95
96	96	96
97	97	97
98	98	98
99	99	99
100	100	100

Thickness Constitution	Run No.	Comparative 13	Comparative 14	Comparative 15	Comparative 16
First layer (μ)	ABC ₁₁₁₁ 14	S ₁ 3	S ₂ 5	S ₁ 24	
Second layer (μ)	a ₃ 3	ABC ₁₁₁₁ 5	a ₃ 30	a ₃ 3	
Third layer (μ)	PVD ₂ 10	PVD ₂ 40	PVD ₂ 10	PVD ₂ 10	
Fourth layer (μ)	a ₃ 3	ABC ₁₁₁₁ 9	a ₃ 5	a ₃ 3	
Fifth layer (μ)	ABC ₁₁₁₁ 30	S ₁ 3	S ₂ 10	S ₁ 20	
Total thickness (μ)	60	60	60	60	

Note:

a₃ - EVA (VAc: 10.3 mole%, MI: 4, mp: 73°C, Vsp: 43°C).

The film of Comparative Run No. 13 caused zigzag whitening phenomena with time in shrinking, and the film of Comparative Run No. 14 had poor processing stability in stretching, tended to puncture and was hard to remove heat of crystallization generated during stretching, because the PVD layer was too thick. Physical properties of small pieces of the sample were measured to obtain results of deteriorated lower-temperature shrinkability, sealability and cold resistance.

4. The film of Comparative Run No. 15 was hard to stretch, and air was introduced into the bubble at 40 to 70°C. to try bubble-up with the result that puncture instantly occurred and stretching could not be carried out at all. The stretching temperature was increased to gradually inflate the bubble, and stretching could be continued in a state of still remaining streaks at a blow-up ratio of about 2 at 80°C with difficulty. At 85°C, the stretching could be continued at a blow-up ratio of 3.5 though with somewhat unstable sway, but stably continued at 91°C at last. The resulting film was opaque and had poor optical characteristics (Haze value: 25%) and lower-temperature shrinkabilities of 5 and 12% respectively at 70 and 80°C. This film was of the type shrinking at high temperatures at last, such as 41% at 95°C, and the shrinkage stress was as low as 90 g/cm². The zigzag whitening phenomenon of the PVDC layer tended to occur when the film was shrunk at 30% or above. Oil resistance was 60 g at 95°C. With increasing stretching

temperature to 95 and 100 °C, deterioration in optical characteristics and reduction in lower-temperature shrinkability tended to be strong. There was a tendency to deterioration in stability of the bubble. When the temperature was further increased, only a locally thin and white elongated film of nonuniform thickness was obtained. and (11). The film of Comparative Run No. 15 was punctured and could not be drawn even at respective temperatures.

4. Brief Explanation of Drawings:

Fig. 1 illustrates temperature dependence of shrinkage factor for films of this invention and commercially available films (a) and (b), wherein

- 1-1: Film of this invention (Run No. 1)
- 1-2: The above-mentioned commercially available film (a)
- 1-3: The afore-mentioned commercially available film (b).

Fig. 2 shows dependence of dart impact strength (with the aforesaid grooved edge adopted) for films of this invention, samples of Comparative example and commercially available films (a) and (b) on measuring temperature.

wherein

- 2-1: Film of this invention (Run No. 1)
- 2-2: Comparative Run No. 6
- 2-3: The above-mentioned commercially available

film (a)

2-4: The aforesaid commercially available film
(b).

Fig. 3 illustrates high-temperature oil
resistance for films of this invention, samples of
Comparative example and commercially available films (a)
and (b),

wherein

3-1: Film of this invention (Run No. 1)

3-2: Comparative Run No. 6

3-3: The above-mentioned commercially available
film (a)

3-4: The aforesaid commercially available film
(b).

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Fig. 1

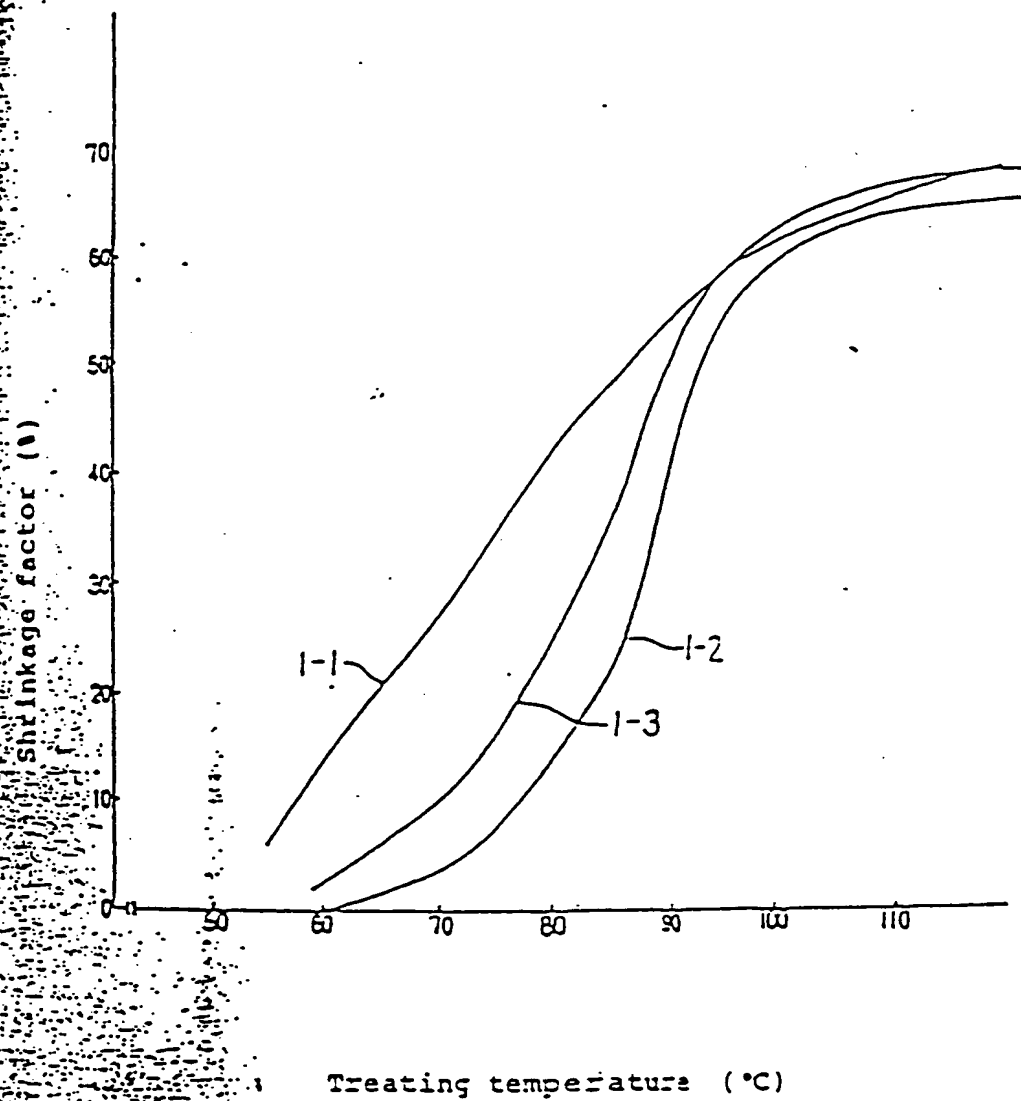


Fig. 2

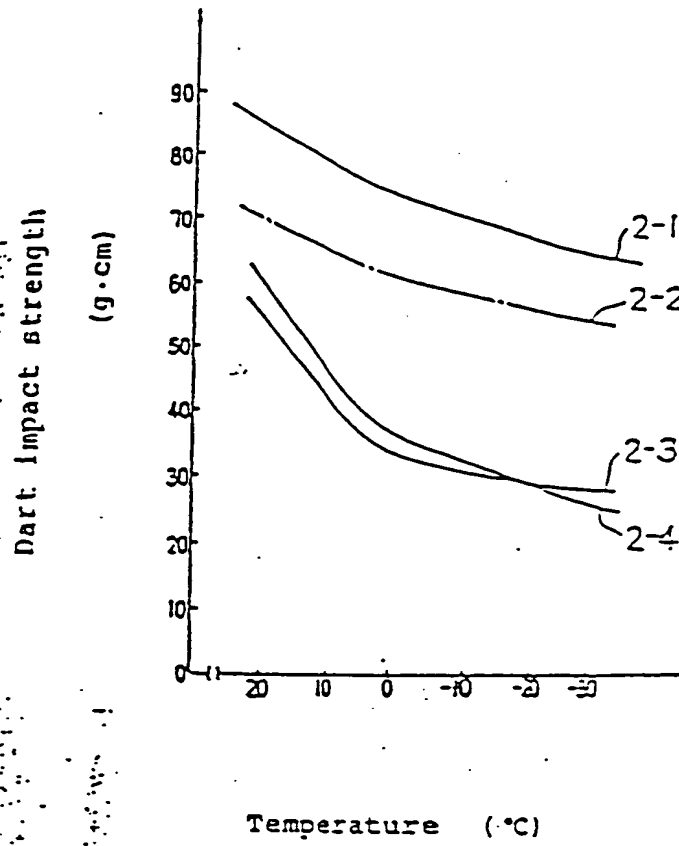


Fig. 3

